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# CALCULATIONS OF THE ELECTRONIC ($4k_F$) AND MAGNETIC ($2k_F$) PHASE TRANSITIONS FROM A HUBBARD HAMILTONIAN WITH AN EXPONENTIALLY DEPENDENT INTERSITE-TRANSFER INTEGRAL

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Résumé - La dépendance exponentielle de l'intégrale de transfert et la corrélation électron-électron $U \geq 3t$ dans l'Hamiltonien de Hubbard conduisent à une séparation des composantes $2k_F$ et $4k_F$ de la transition de phase Peierls. Un diagramme de phase des températures de transition vers la valeur de U/t peut être construit. Les résultats calculés pour quelques propriétés physiques peuvent être comparés favorablement avec les résultats des expériences.

Abstract - An exponential intersite-dependence of the transfer integral in the Hubbard Hamiltonian together with $U \geq 3t$ in a quarter filled band lead to a separation of the $2k_F$ and $4k_F$ components of the Peierls transition. A phase diagram of the transition temperatures versus U/t can be constructed. The results for some physical properties such as the spin susceptibility can be favorably compared with experiment.

## Introduction

Recently we published (1) a technique to calculate electronic Peierls and spin Peierls phase transitions from a simple Hubbard model, in which the transfer integral was taken to depend exponentially on the intersite distance. Basically the method solves for the eigenvalues of the Hubbard Hamiltonian and with a partition function we then calculate the electronic free energy. A lattice energy term is added and minima of the free energy as a function of temperature are found by allowing the system to distort with $4k_F$ and $2k_F$ distortions for a quarter filled band and $2k_F$ and $k_F$ distortions for a half filled band. Cooperativity is ensured by requiring that all members of the ensemble, which the free energy calculation implicitly requires, show the same distortions at the same time. For details of the calculation and its group theoretical justification we refer to our earlier work (1).

The calculation was carried out on a ring of four atoms with two electrons (quarter-filled band) and it was considered somewhat surprising that such a limited system should already exhibit the phase transition features so clearly. It was therefore decided to extend the calculation to a ring of 8 atoms with 4 electrons to see whether the original results would be affected by ring size. Also, since for a 4/8 system we consider 1860 states, the discretion - always a problem in finite systems - will be less, which may allow us to use our computational results at lower temperatures. Finally we performed a calculation on a system of 4 atoms with 4 electrons (half filled band) for which the results were fitted to experiment.

## The Model and the Calculation

Although most details of model and calculation have been given elsewhere (1) it is useful to summarize some of them here. The electronic system is described by the Hubbard Hamiltonian:

$$H = - \sum_{\substack{1 \neq m \\ \sigma}} t_{1m} c^{\dagger}_{1,\sigma} c_{m,\sigma} + \sum_{1} U n_{1,\sigma} n_{1,-\sigma},$$

where l and m label the sites, $c^{\dagger}_{l,\sigma}$ and $c^{\dagger}_{l,\sigma}$ are the usual creation and annihilation operators for an electron with spin σ at site l, and $n_{i,\sigma}$ is the number operator $c_{i,\sigma}c_{i,\sigma}$. As a basis set we take the $m_s = 0$ two electron states

$c_{l\sigma},c_{m\sigma}|0\rangle$ for the 2 electron system and

$c^{\dagger}_{l\sigma}c^{\dagger}_{m\sigma}c^{\dagger}_{n\sigma}c^{\dagger}_{p\sigma}|0\rangle$ for the four electron systems

which is permitted in the absence of a magnetic field and spin-orbit coupling. To facilitate the calculation we formed linear combinations which were bases for the irreducible representations of the group $C_{2v}$. Inspection of the parity of the spin part of the linear combinations divides these up in 336 singlet states, 1134 triplet states and 350 quintet states for the 4/8 system. The eigenvalues of this Hamiltonian were obtained numerically in terms of U/t. For a quarter-filled band (4/8 system) the $4k_F$ and $2k_F$ distortions, described by the order parameters ξ and η, respectively are indicated in figure 1.

The electronic free energy was found by computing $F_{el} = -kT \ln Z_{el}$, where the partition function $Z_{el} = \Sigma_i g_i \exp - \varepsilon i/kT$, the summation running over all the eigenvalues $\varepsilon_i$.

The free energy of the lattice repulsion was obtained from $F_{lat} = B\Sigma_j r_j^{-n}$, j running over the sites, thus neglecting lattice entropy. A reasonable estimate for B can be obtained from the lattice compressibility. The value of n was taken to be 12, but could be varied when used to fit experimental data.

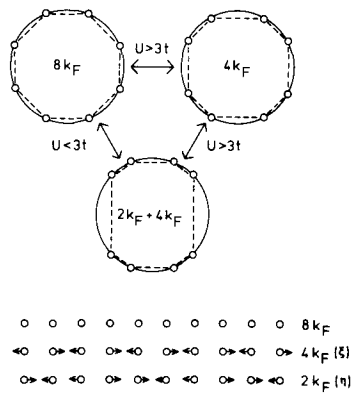


Fig. 1. Conformations of the sites in the regular ($8k_F$), dimerized ($4k_F$) and quartermerized ($2k_F + 4k_F$) phases for a quarter-filled band (4/8 system).

Central to our calculation is the exponential variation of the transfer integral with inter-site separation: $t(:) r^3 \exp -cr$. Apart from the fact that one would expect this type of variation for the transfer between p-functions at a separation of about 3 - 3.5 A from a calculational point of view, it turns out that the exponential t-dependence is crucial to the occurrence of a $4k_F$-distortion in a quarter-filled band system.

The computation, although lengthy for a 4/8 system, is now straightforward. After calculating the eigenvalues, the total free energy is obtained as a fuction of the $4k_F(\xi)$ and $2k_F(\eta)$ - distortion parameters and the temperature. Then the minimum of $F(\xi,\eta)$ at a given temperature is found. By executing the computation for various values of U/t we can then construct a phase diagram of the phase transition temperatures vs U/t.

Since we know the complete electronic partition function many other properties can be calculated as well. The spin susceptibility is evaluated from $\chi_{reduced} = \chi \frac{6t_o}{Ng^2\beta^2} = \Sigma S_i(S_i+1) \frac{g_i \exp(\varepsilon_i - \varepsilon_o)/kT}{N_{el}.Z.T}$

where the summation runs over the triplet and quintet states. The intensities of singlet-singlet and triplet-triplet optical transitions can also be found from the oscillator strength:

$$f_{i\to j} = (\varepsilon_i-\varepsilon_j)g_i \frac{1}{Z}\{\exp-(\varepsilon_i-\varepsilon_o)/kT - \exp - (\varepsilon_j-\varepsilon_o)/kT\} M_{i\to j}^2$$

where $\vec{M}_{i\to j} = \Sigma_k c_{ik} c_{jk} \vec{R}_k$, where $\vec{R}_k$ is the position vector of site k and $c_{ik}$ and $c_{jk}$ the coefficients of the eigenfunctions i, j at the site K. The "pressure dependence" of a transition temperature can also be obtained. Pressure decreases the total size of the ring by Hooke's law:

$dR_o/dP = -\gamma R_o$

which has a strong effect on the transfer integral for the undistorted phase, since it is exponentially dependent on the inter-site distance. The on-site electron-electron repulsion U, being largely a molecular quantity was assumed to be independent of pressure. Since the calculations were all performed in units $t_o^o$, the transfer integral at zero pressure of the undistorted chain, care was taken to finally readjust all calculated quantities from $t_o^p$, in which they are computed, to $t_o^o$ to be able to compare them to one another.

## Results

### Quarter-filled bands

To our surprise the results obtained for the 4/8 (4 electrons on 8 sites) system did not differ much from those on the 2/4 system, indicating that convergence (at least for higher temperatures) is apparently reached fairly quickly for the number of states required by the Hubbard Hamiltonian. Figure 2 gives the phase diagram of $T_c$ vs U/t, compared with the 2/4 calculation and certainly qualitatively the results are identical.

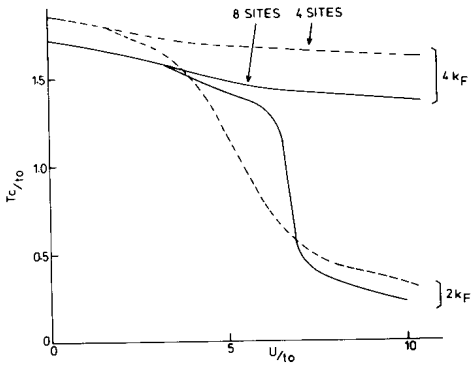


Fig. 2. Reduced transition temperatures ($T_c/t$) versus U/t for the 4/8 system (drawn line) and the 2/4 system (dotted line), i.e. quarter filled bands.

At U/t = 0 the Peierls transition consists of $2k_F$ and $4k_F$ components, and at U/t > 3 (somewhat higher than in the 2/4 system, where this value was about 1) the $4k_F$ component is split off. The $4k_F$ transition temperature is then insensitive to U/t, while the $2k_F$-transition temperature rapidly decreases, as would be expected for a spin-Peierls transition, which is driven by the variation of the exchange energy J, which itself decreases with increasing U/t, as long as we realize that an approximation for J is obtained from $J = 2t^2/U$. It should be noted that our 2/4 calculation also yielded a pure $2k_F$ distortion, which was particularly significant at U = 0. To calculate this distortion we would have to transform all our wave-functions, since the $C_{2v}$ axes system is then quite different. Since there will, in general, always be a finite value of U, we did not consider it worthwhile to calculate the pure $2k_F$ phase for the 4/8 system as well. There seems to be no doubt, however, that the phase will exist.

The variation of the spin susceptibility with temperature is given in fig. 3, and again it is similar to that obtained earlier, be it that it should be reliable to lower temperatures, the discretion of the calculation now being less.

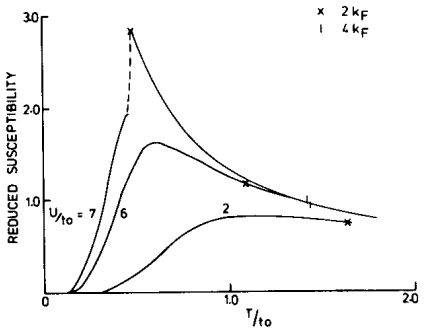


Fig. 3. Variation of the reduced spin susceptibility in a quarter-filled band as a function of reduced temperature for various values of U/t in the 4/8 system.

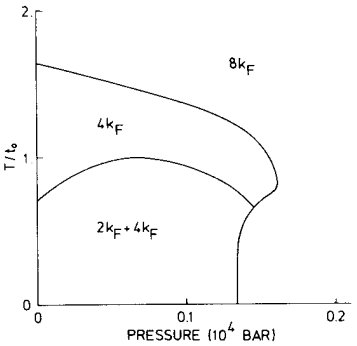


Fig. 4. The reduced phase transition temperatures ($T_c/t_o$) versus pressure for a quarter-filled band (2/4 system). The pressure axis was obtained from a relative change in $R_o$ and a compressibility of $4.10^{-11}$ cm$^2$/dyne.

The pressure dependence is given in fig. 4. It will be clear that the $4k_F$ transition goes down, while the $2k_F$ transition goes up for our choice of parameters, in good agreement with the experimental results of Bloch et al. (2). The $4k_F$-dependence is easy to understand. Pressure increases $t_o$, therefore decreases $U/t_o$. Looking back at fig. 2, we see that $T_c(4k_F)/t_o$ is almost independent of $U/t_o$, therefore as p and thus $t_o$ increase $T_c$ ($4k_F$) goes down. For $T_c(2k_F)$ the situation is more complicated. As $t_o$ increases, $U/t_o$ decreases and from fig. 2 it is clear that $T_c(2k_F)/t_o$ increases. It now depends on such details as whether $T_c(2k_F)/t_o$ goes up faster than $t_o$. Obviously, this will depend on the actual value of $U/t_o^o$. The best estimates we can make for U, $t_o^o$ and the lattice stiffness indicate that we are in about the right parameter range, but no hard and fast statement can be made. It is finally the increase of the lattice stiffness, which makes aIl the phase transitions disappear, but the sudden drop we compute at higher pressures is undoubtedly a result of the discretionary nature of our calculation, it must be considered an artifact.

Half-filled Bands

Encouraged by the stable results of the quarter filled band calculation we decided to also investigate a 4/4 system, i.e. a half-filled band with 4 electrons on 4 sites (70 states). Basically, this is a simpler problem, since only one ($2k_F$) phase transition is expected. At low U/t this is an electronic Peierls,at high U/t this should be considered a spin Peierls transition. The calculation proceeds in exactly the same manner as for the quarter filled band. Fig. 5 gives the phase diagram, disclosing indeed one transition, which decreases with increasing U/t as might be expected again for the decreasing $J \approx 2t^2/U$. The variation of the spin susceptibility with temperature for various values of U/t is given in fig. 6. It will be clear that higher values of U/t lead to a more first order nature of the phase transition. This was also found from a study of the temperature dependence of the $2k_F$ order parameter. A calculation of the intensity of the so-called charge-transfer transition as a function of t was also performed, the result is given in fig. 7. It is clear that its increase in intensity, when

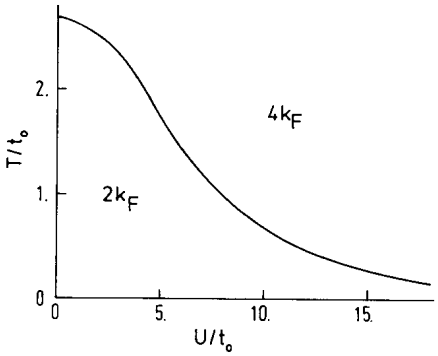


Fig. 5. Reduced transition temperatures versus U/t for the 4/4 system, i.e. a half-filled band.

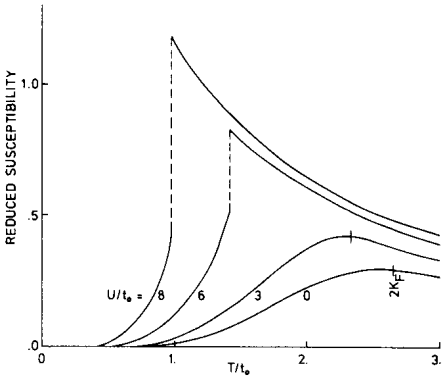


Fig. 6. Variation of the reduced spin susceptibility with the reduced temperature for various values of U/t in a half-filled band.

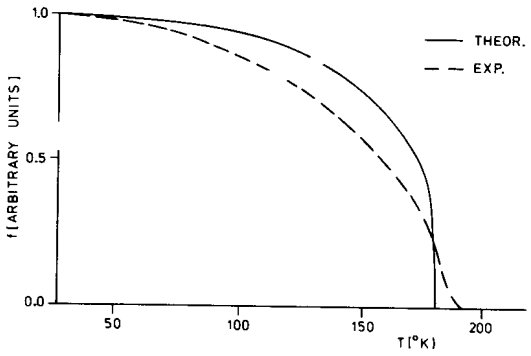


Fig. 7. Comparison of the calculated and experimental (13) strength of the charge-transfer absorption in Wurster's Blue perchlorate as a function of temperature The parameters used are given in table I.

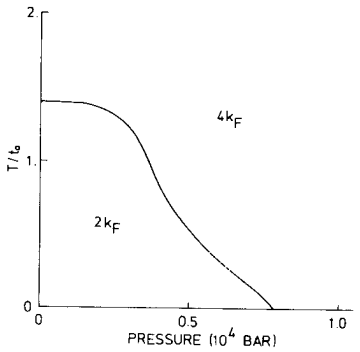


Fig. 8. The reduced transition temperature ($T/t_o$) versus pressure for a half-filled band (see fig. 4).

going to lower temperatures is entirely due to the increase in the transfer integral within the dimer being formed in the transition. It should be noted that in real systems the intensity of this transition is - through this intra-dimer interaction - stolen from the intra-molecular absorptions, as is obvious for instance in Würster's Blue Perchlorate (3). The pressure dependence of the transition temperature (divided by $t_o$!)is given in figure 8. As p increases, $t_o$ increases, $U/t_o$ decreases and $T_c/t_o$ increases. Whether this will increase or decrease $T_c$ again depends on details. In general, one would expect $T_c$ first to go up and then to go down with increasing pressure. At high p the lattice becomes so stiff as to not further permit the transition. Obviously, one would also expect a magnetic field to have an effect on the transition temperature. But it introduces new phase transitions as well, as was predicted earlier by Bray et al. (4), by Cross (5) and by Bulaevski (6). In our simple case the effect of a high magnetic field amounts to uncoupling two of the four spins. These two lose their binding and a ($k_F + 2k_F$)-phase is formed. Figure 9 gives the results of our calculation, clearly showing the change in the phase diagram. It is tempting to believe that the recently obtained results by Bloch et al. on the anomalous behavior of the magnetic moment at high magnetic fields (7,8) in TTF-BDT (Cu) and MEM $(TCNQ)_2$ are indicative of the formation of such magnetically induced phases.

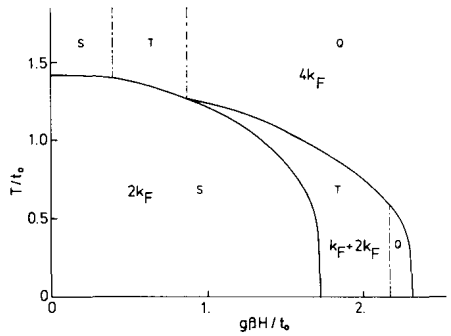


Fig. 9. Effect of a magnetic field on the reduced phase transition temperature. for a half-filled band. Note the now induced ($k + 2k_F$) phase. The ground state magnetic character is in the relevant ranges indicated by S(singlet), T(triplet) or Q (quintriplet).

Often, in the literature the frequency of the charge-transfer transition is taken as an indication of the value of U. We investigated this problem and in fig. 10 we give a plot of $\Delta E_{ct}/t_o$ vs $U/t_o$. It will be clear that for $U/t_o \approx 6$, which seems a reasonable estimate for most materials, this assumption can be wrong by a factor of 2! Finally, we made an effort to compare our computational results with experiment, in particular as regards the spin susceptibilities. For some simple TCNQ salts these are available, they show an increase as a function of temperature (9). This means we are in a region of fairly low temperatures. Because of the discretionary nature of the calculation, computed values should not be taken too seriously. Nevertheless, reasonable fits to experiment were obtained with the parameter values given in Table I. More details about these values can be found in a forthcoming paper (10), here we just want to point out, that for $CR_o$, describing the steepness of the transfer integral variation, we had to use a value of 5.8 - 6.6, instead of 10, as used in our model calculations. The earlier value was derived from a computation of two p-functions separated by $R_o \cong 3.3A$ and being moved along their common axis. In TCNQ salts the distortion generally appears to be a sliding motion, where the p-function overlap is changed at right angles to their common axis. We then indeed expect a less steep dependence on the now generalized coordinate R. A lot of work has been carried out in the past on the half-filled band system Würster's Blue perchlorate ($TMPD^+ ClO_4^-$). In this system accessible temperatures show both an increasing $\chi$ below $T_c = 186$ K and a decreasing (Curie-like $\chi$ above $T_c$.

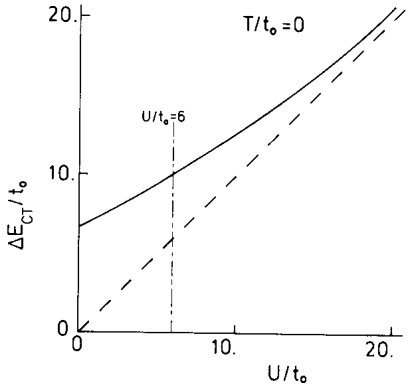


Fig. 10. $\Delta E_{ct}/t_o$ versus $U/t_o$, see text

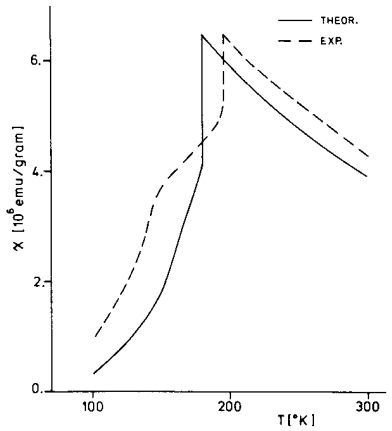


Fig. 11. Comparison of the experimental (11) and theoretical spin susceptibilities of $TMPD^+ClO_4^-$.

In this case our calculation is quite adequate, as can be seen in fig. 11, where we compare the experimental and calculated susceptibilities of $TMPD^+ClO_4^-$ for the parameter values given in table I. The agreement is very satisfying. The high value of $CR_o$ can be understood, since in this compound the relative motion of the $TMPD^+$ is longitudinal (12). Finally in figure 7, we compare the experimental (13) and theoretical charge transfer absorption intensities for the same parameter values. Again the agreement is very satisfactory.

Table I. Fitting parameters for some half-filled band systems.

| | $U/t_0$ | $CR_0$ | U(eV) | $t_0$(eV) | $T_c$(°K) | $T_{c,exp}$(°K) | $A/t_0$ |
|---|---|---|---|---|---|---|---|
| TMPD $C10_4$ | 40.0 | 9.0 | 1.00 | 0.025 | 190 | 196 | 17 |
| NaTCNQ | 6.0 | 6.5 | 2.27 | 0.38 | 305 | 345 | 160 |
| KTCNQ | 6.0 | 6.6 | 1.72 | 0.29 | 367 | 396 | 160 |
| RbTCNQ (II) | 4.0 | 6.0 | 1.08 | 0.27 | 238 | 220 | 160 |
| CsTCNQ | 4.0 | 6.0 | 0.88 | 0.21 | 195 | 217 | 160 |
| RbTCNQ (I) | 3.0 | 5.8 | 0.76 | 0.25 | 282 | 310 | 160 |

Conclusions

The phase transitions and some of the physical properties of TCNQ salts and related substances can be understood on the basis of a Hubbard Hamiltonian with an exponentially varying transfer integral. It seems,in general, sufficient to consider four sites with two electrons (quarter-filled) or with four electrons (half-filled band). When the temperatures considered are higher than the

discretionary nature of the bands ($T \geq 0.3\ t_o$) the results can be directly compared with experiment. At lower temperatures, much more care should be exercised, but qualitatively the results still apply.

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